Production of Polycyclic Aromatic Hydrocarbons from Underventilated Hydrocarbon Diffusion Flames

M.P. Tolocka and J.H.Miller
Department of Chemistry
The George Washington University
Washington, DC 20052

Introduction

Polycyclic Aromatic Hydrocarbons (PAH) are ubiquitous products of incomplete combustion, and have been found adsorbed on the particulate emissions from wood fires [1], pulverized coal combustion [2], waste incineration [3,4,5], and laboratory scale flames [6,7]. Because specific PAH are known to be mutagenic [8], measuring the concentration levels of these compounds is important in assessing risk from these combustion sources.

It has been recently noted [9] that soot generated from underventilated diffusion flames is remarkably different in structure than soot from overventilated combustion, and the smoke generated from underventilated combustion has a much higher organic composition. It is expected that the organic component of the soot is largely PAH, molecules which are thought to be the precursors to soot formation [10]. We present here initial quantitative measurements of PAH adsorbed on the surface of particles generated from overventilated and underventilated flames.

Experimental

The flames studied are supported on an axi-symmetric burner which consists of a 0.25 inch diameter fuel tube surrounded by a 0.75 inch diameter co-flow. The burner is connected to a six-way diagnostics cross that can be equipped for *in-situ* or extractive sampling diagnostics. This cross is connected to a one inch diameter, 25 inch long quartz tube enclosed by a tube furnace (not used in these experiments). Above this is another six way diagnostics cross, which leads to the ventilation system. The experiment is shown in Figure 1. Because the system is isolated from the laboratory environment, the air or fuel flow can be varied to change the global equivalence ratio (GER) defined as the moles of fuel divided by the moles of oxygen in the system normalized by the stoichiometric ratio. Natural gas and natural gas doped with toluene were used as the fuels. The latter was chosen because of its higher expected soot yield [11].

Natural gas was burned at a flow rate of 1.0 cm³/sec and doped with toluene at approx. 3 mole percent, and the air flow was varied to change the GER. At each GER, a 3 mm orifice Pyrex probe was inserted into the upper diagnostics cross and post-flame gases were withdrawn through a 2.4 cm glass fiber filter with a pore size of 1.0 μm, which had been dried and weighed before introduction into the sampling system. Once the soot was collected, the filter was removed and immediately rinsed with dichloromethane, dried thoroughly to constant weight. The net soot weight was calculated from the differences between the weighed filter and the particulate-collected filter. The filter was Soxhlet extracted with 250 ml of dichloromethane for 24 hours. The resultant extract was taken up in 2 ml of dichloromethane/benzene (50/50 vol. %) solution. The sample collection protocol was repeated at each global equivalence ratio (GER = 0.6 to 1.8) for both flames, and for a blank filter. Qualitative analysis of each extract was performed using the GC/MS in the SCAN mode and mass spectra were compared to the NIST database of mass spectra. Quantification of the emitted polycyclic aromatic hydrocarbons as a function of GER was accomplished utilizing the GC/MS detection operating in the SIM mode. The selected masses monitored were: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene, and fluoranthene which ranged in mass from 128 to 202 amu. An external standard of 16 PAH was used to compute response factors for the selected PAH, ranging in size from 2 to 4 rings at specific retention times. The response factor of these PAH, R_f, can be calculated using the following:

$$R_f = \frac{m_c}{A_i}$$

where m_c is the mass of the component in the standard sample and A_i is the integrated area of the chromatographic peak. The resultant concentration of ith species, C_i, in milligram of analyte per kilogram of soot (mg/kg), can be expressed as:

$$C_i = \frac{[A_i \times V_t \times R_f]}{m_s}$$

where V_t is the total volume of the extract and m_s is the mass of soot collected on the filter.

Results and Discussion

Results from the quantitative GC/MS analysis of the sampled particulate are presented in Figures 2 and 3. Plots are shown for eight quantified PAH species (expressed as mg PAH per kg soot) for each fuel as a function of GER. These results indicate that the amount of each individual PAH as a fraction of particulate increases exponentially as a function of GER, with an average slope for all eight species of 1.13 (± 0.21 at 99 % confidence). That is, for a unit increase in GER, there is approximately an order of magnitude increase in the fraction of each PAH contained in the smoke. In the previously cited study[9] Leonard *et al.* report that from underventilated methane flames supported on a burner similar to ours in design, the organic fraction of particulate at GER=2.0 is 63% and 90% at GER=4.0. Further, data collected by Graham *et al.* [3] demonstrated a ten-fold increase of fluorene and naphthalene after a decrease in the oxygen concentration in a high temperature reactor from overventilated to stoichiometric conditions.

Figure 4 shows the sum of these 8 PAH yields, as mass fraction of collected particulate, again showing the exponential dependence of PAH concentration on GER. Also displayed on the figure is the measurement of the ratio of organic to elemental carbon found in particulate generated by methane/air flames studied by Leonard *et al.* [9]. The sparse Leonard data are qualitatively similar to our data: an increase in the organic fraction of particulate observed with increasing GER. The overall levels of total PAH observed here are lower due to the fact that the organic fraction measured in the cited study contains other hydrocarbon species that are not included in our quantification. This result has the implication that at GERs > 1.0, the chemistry of the soot is significantly influenced by the chemistry of PAH adsorbed on the smoke particulate. This is also supported by the qualitative runs where the chromatograms became more complex as the GER increased. The matrices taken from GERs > 1.4 included oxygenated species such as: naphthalaldehyde, dibenzofuran, 9H-fluorene-9-one, and 9,10 anthraquinone. Furthermore, the extract was fractionated on an alumina column with hexane, benzene, methyl chloride and methanol. The methanol fraction was analyzed *via* FTIR and displayed prominent absorption features ca. 1700 cm^{-1} and 3400 cm^{-1} indicative of carbonyl and OH stretch, respectively. It is also important to note that doping natural gas with toluene results in 11 to 13 times more PAH than the pure natural gas flame. In a previous study, Olson *et al.* [12] found for rich premixed ethylene flames that a dramatic increase in PAH was observed when toluene was added to the fuel stream, thus increasing the aromatic content and leading to PAH growth and hence, soot production.

In order to quantify the mass of PAH found in the soot per unit mass fuel burned, an estimation of the smoke yields from our flames was necessary. In the experiments performed by Leonard *et al.* [9] smoke yields for methane and ethylene flames were reported over a large GER range (0.5 to 4.0). For our data, it was assumed that the natural gas flame and the natural gas/toluene flame were analogous to methane and ethylene flames, respectively. The Leonard *et al.* data was fit to a 3rd order polynomial to interpolate the smoke yield at the GERs studied here. In Figure 5 total PAH yield per unit mass fuel (in mg PAH per kg fuel) reveals the same exponential increase in the total amount of PAH as found in Figure 4. Again, more PAH per unit fuel is found when toluene is added to the fuel which was seen previously in the work done by Hamins *et al.* [11] on toluene destruction in non-premixed methane-toluene/air flames.

Conclusions and Future Directions

The evidence presented here suggests that the chemistry of soot generated from underventilated combustion should be influenced by the PAH adsorbed on the surface of the particles. Also, in environments where combustion conditions can become underventilated such as incinerators or room fires, levels of PAH can be significantly higher than those found in overventilated conditions. Future work will include monitoring the changes in amount and type of PAH adsorbed on soot as it oxidizes. Also, we will compare the underventilated combustion of other fuels such as ethylene and propane to these results.

Acknowledgments

References

1. S.B. Hawthorne, D.J. Miller, J. Langenfeld, and M.S. Krieger, *Environ. Sci. and Tech.* 26, 2251-2262 (1992)
2. C.A. Miller, R.K. Srivastava, and J.V. Ryan, *Environ. Sci. and Tech.* 28, 1150-1158 (1994)
3. J.L. Graham, D.L. Hall, and B. Dellinger, *Environ. Sci and Tech.* 20, 703-710 (1986)
4. J.H. You, P.C. Chiang, K.T. Chang, and S.C. Chang, *Journ. Haz. Mat.* 36, 1-17 (1994)
5. K. Yasuda, M. Kaneko, K. Sugiyama, H. Yoshino, and Y. Ootsuka, *JAPCA* 39, 1557-1561 (1989)
6. J. Marr, D.M. Allison, L.M. Giovane, L.A. Yerkey, P. Monchamp, J.P. Longwell, and J.B. Howard, *Combust. Sci. and Tech.* 85, 65-76 (1992)
7. B.A. Benner, N.P. Bryner, S.A. Wise, G.W. Mulholland, R.C. Lao, and M.F. Fingas, *Environ. Sci. and Tech.* 24, 1418- 1427 (1990)
8. J.R. Blakeslee, A.M. Elliot, and L.J. Carter Polycyclic Aromatic Hydrocarbons: Formation, Metabolism and Measurement, M. Cooke and A.J. Dennis (ed.) 123-134 (1983)
9. S. Leonard, G.W. Mulholland, R. Puri, and R.J. Santoro, *Combustion and Flame* 98, 20-34 (1994)
10. M. Frenklach, D.W. Clary, W.C. Gardner, and S. Stein, *Twentieth Symposium (International) on Combustion (The Combustion Institute)* 887-901 (1984)
11. K. L. Olson, S.J. Harris, and A.M. Weiner, *Combust. Sci and Tech.* 51, 97-102 (1987)
12. A. Hamins, D.T. Anderson, and J.H. Miller, *Combust. Sci. and Tech.* 71, 175-195 (1990)
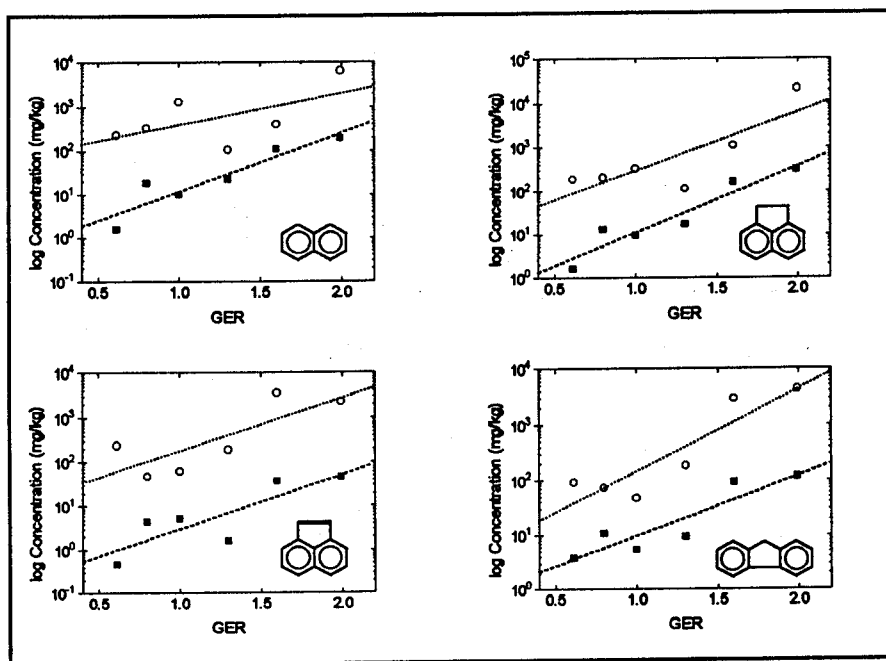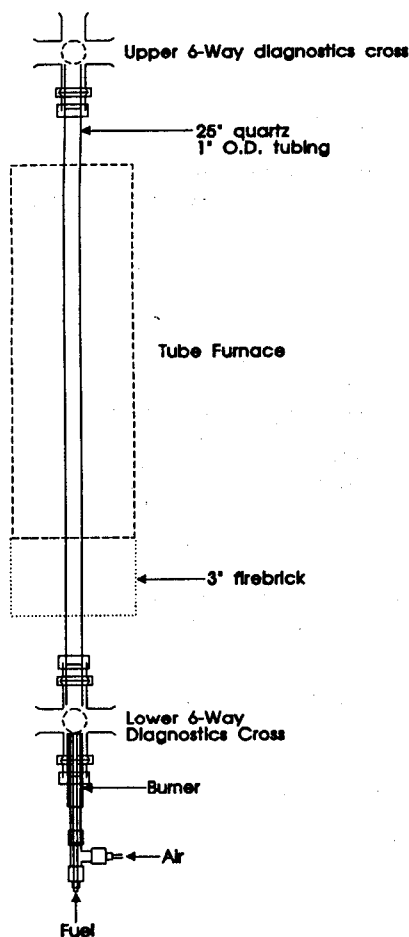
Figure 1. Experimental Apparatus

Figure 2. GC/MS monitored PAH. Each plot is an individual PAH concentration (mg per kg soot) versus GER. A. Naphthalene B. Acenaphthylene C. Acenaphthene D. Fluorene. (O) Data are from the natural gas/toluene flame. (■) are from the natural gas flame.
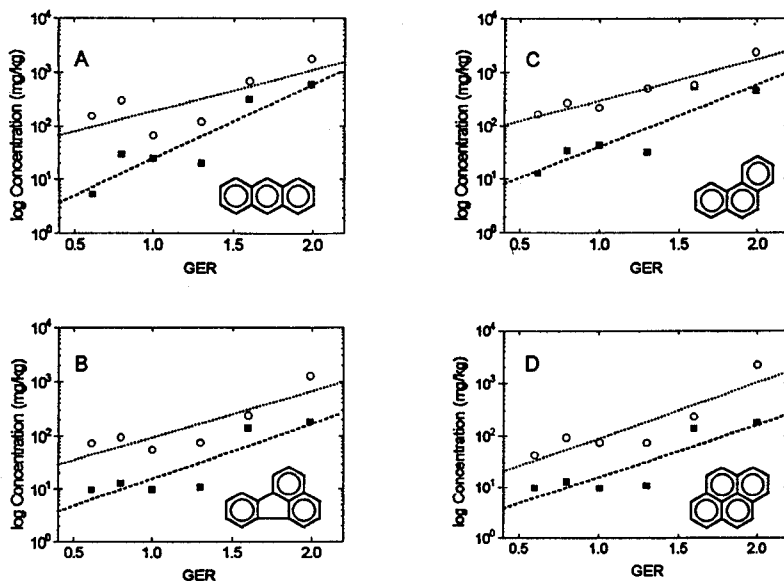
255

Figure 3. GC/MS monitored PAH. Each plot is an individual PAH concentration (mg per kg soot) versus GER. A. Anthracene B. Fluoranthene C. Phenanthrene D. Pyrene (O) data are from the natural gas/toluene flame. (■) are from the natural gas flame.

Figure 4. Summary of total PAH concentration as a function of GER. (▲) Data taken from Leonard *et al.* (1994). All data in units of (mg PAH per kg soot)
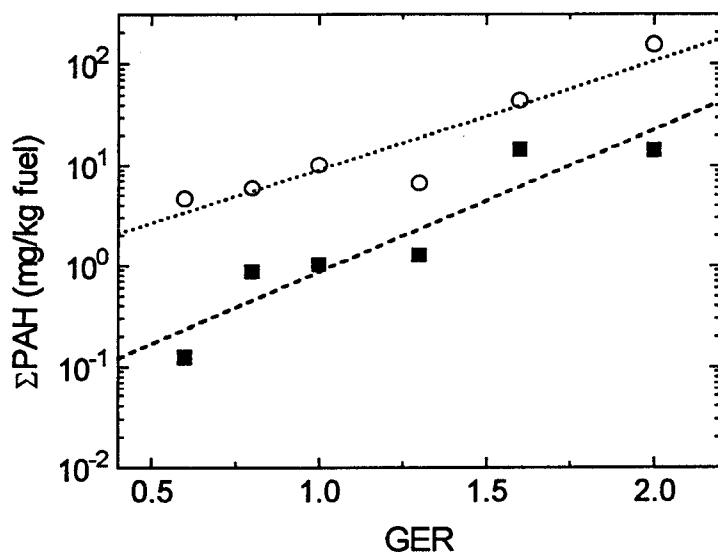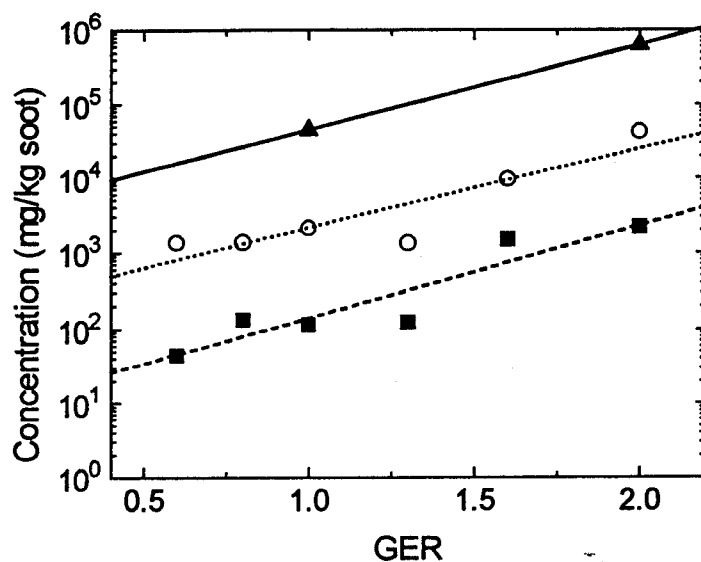

Figure 5. PAH (mg PAH/kg fuel) yield per unit mass of fuel.